Isotope Hydrology

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Abstract Environmental isotopes were introduced into the study of hydrological cycle during the mid-nineteenth century as complementary tools to existing methods like geology, geochemistry, geophysics, etc. for addressing problems pertaining to movement of water, pathways of streams, residence times of groundwater, etc. However, the applications of environmental isotopes as potential tools to unravel many hidden processes and factors governing water, its source and dynamics in all stages of hydrological cycle have gained momentum after the introduction of advanced instruments for isotope measurement of water. In recent times, the critical information that is being obtained from isotopic tools is precipitation contribution to groundwater, efficacy of recharge structures for augmenting groundwater supplies, source and mechanism of groundwater contamination and its transport, sustainability of deep groundwater, etc. The common isotopes that are widely used include ²H, ¹⁸O, ¹³C, ¹⁵N and ³⁴S which are stable in nature and ²²²Rn, ³H and ¹⁴C, which are radioactive in nature. While stable isotopes help in understanding the source and mechanism of groundwater recharge based on their natural distribution over space and time, the radioisotopes help in understanding the groundwater residence times and dynamics of any given water system due to their inherent radioactive decay.

Keywords Environmental isotopes · Oxygen-18 · Deuterium · Tritium · Carbon-14 · Global meteoric water line

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1 Introduction

Isotope hydrology is an emerging discipline with expanding investigation tools for many environmental problems. Naturally occurring elements in water comprise about 1700 stable and unstable (radioactive) isotopes, commonly referred to as environmental isotopes. Globally distributed isotopes produced from anthropogenic sources, such as aboveground nuclear detonation testing and emissions from nuclear reactors, are considered environmental isotopes. The use of artificial isotopes in hydrology has markedly declined because of perceived concerns about injection of foreign substances into water supplies. An important misconception on the use of environmental isotopes for hydrology persists and needs correction before proceeding. There is the perception that one needs to 'manually' inject isotopes into the environment to study their attributes in the subsurface. This is simply untrue, and the entire measurements and interpretations of environmental isotopes are predicated on isotopes occurring naturally in the hydrosphere, originating from cosmogenic nuclide production, or occur as persistent anthropogenic releases into the hydrosphere. Next, while isotopes behave as tracers of hydraulic processes, they also behave as carriers, describing physiochemical changes during fluid, solid, and gas transformations. The limited capability of chemical compounds including dyes, gases, and also particulate tracers, which are still employed (Sanford et al. [1996](#page-34-0)) as collaborative tools, preceded the advent of environmental isotope applications. Today the terms isotope and tracer are commonly used as synonyms in the scientific community. The progression of isotope techniques in hydrology is rather analogous to the present wide acceptance of numerical modelling in groundwater hydrology following the advancement of microprocessors in portable computers. With further analytical achievements and more publications in practical applications, it is expected that isotope techniques will also become an integrated part of most hydrological investigations.

2 Basic Isotope Concepts

A nuclide is defined in terms of the number of protons and neutrons that make up its nucleus. Isotopes are nuclides with the same atomic number (proton number) but with different numbers of neutrons. About 26 nuclides are stable among the nearly 1700 nuclides (Walker et al[.1989](#page-35-0)), which have been discovered. However, most nuclides are not stable but are radioactive and decay spontaneously until they achieve a stable nuclear configuration.

2.1 Stable Isotopes

There are natural variations in the ratios of the stable isotopes of many elements. Isotope ratio differences in materials containing hydrogen (²H/¹H usually written as D/H), carbon (¹³C/¹²C), nitrogen (¹⁵N/¹⁴N), oxygen (¹⁸O/¹⁶O) and sulphur (³⁴S/³²S) have potential uses in various hydrological studies.

Among the low atomic number or 'light' isotopes, fractionation may occur. Isotope fractionation is the partitioning of isotopes by physical or chemical processes and is proportional to the differences in their masses. Physical isotopic fractionation processes are those in which diffusion rates are mass dependent, such as ultrafiltration or ion and molecular diffusion. Chemical isotopic fractionation processes involve redistribution of isotopes of an element among phases or chemical species. Chemical fractionation effects occur because a chemical bond involving a heavier isotope will have lower vibrational frequency than the equivalent bond with a lighter isotope. Generally, in equilibrium isotopic reactions, heavy isotopes are enriched in the compound with the higher oxidation state. Fractionation may occur during both equilibrium and irreversible chemical reaction. During irreversible chemical reaction, kinetic fractionation processes, the lighter, i.e. lower atomic mass, of two isotopes of an element will form the weaker and more easily broken bond. The lighter isotope is more reactive; therefore it is concentrated in reaction products, enriching reactants in the heavier isotope.

2.1.1 δ Definition

It is difficult to determine accurately the absolute isotope values in every compound through routine analysis. Fortunately for most isotope geochemical studies, it is sufficient to know the relative abundance with respect to standard value. These relative isotope concentrations can be determined easily with great accuracy by a differential isotope ratio measurement using double-collecting mass spectrometers. The relative difference is called *δ* value and is defined as

$$
\delta = \frac{R - R_{\text{std}}}{R_{\text{std}}}
$$

where *R* represents the isotope ratio of a sample $(^{2}H/^{1}H, {}^{13}C/^{12}C, {}^{18}O/^{16}O,$ etc.) and *Rstd represents the corresponding ratio in a standard. The* δ *value is generally* expressed in parts per thousand (per mil, ‰) and written as

$$
\delta = \frac{(R - R_{\text{std}})}{R_{\text{std}}} \times 10^3
$$

2.1.2 Standards

The selection of standards for reporting stable isotope data is very important in environmental isotope geochemical work for comparison of results obtained from different laboratories. The International Atomic Energy Agency is presently coordinating the preparation, calibration and distribution of internationally acceptable standards for use in hydrological investigations.

Standard mean ocean water (SMOW) is used as the standard for measurement of ¹⁸O and ²H in waters. It corresponds to hypothetical water having ²H/¹H and ¹⁸O/¹⁶O isotopic ratio equal to mean isotopic ratio of ocean waters. PDB is the universally accepted 13C standard. PDB refers to calcium carbonate of the rostrum of a cretaceous belemnite from Pee Dee Formation in South Carolina, USA. PDB standard has long been exhausted, and IAEA panel in 1983 (Gonfiantini [1983\)](#page-33-0) adopted NBS-19 new standard, supplied by the US National Bureau of Standard and is now known as the National Institute of Standards Technology (NIST), to define the new VPDB (Vienna PDB) scale as follows:

$$
\delta^{13}C_{\text{NBS19/VPDB}} = +1.95\%
$$

The accepted reference standard is CDT which is the triolite phase (FeS) from the Canyon Diablo meteorite. It has a ratio of $34S/32S = 22.22$. The IAEA is supplying a secondary sulphur standard called OGS (IAEA [1984](#page-33-1)). This is a BaSO4 precipitated from ocean water sulphate. OGS has a $\delta^{34}S$ (SO4^{2−}) value of about +20‰ with respect to CDT. Atmospheric nitrogen is used as working and reference standard by most of the laboratories. Atmospheric nitrogen (AIR) comes from well-mixed reservoir with a very reproducible mass ratio of 3.677×10^{-3} . IAEA is supplying two samples of ammonium sulphate as secondary standard.

2.2 Radioactive Isotopes

Most isotopes are unstable and become increasingly unstable as the number of neutrons increases or decreases outside the stability zone of nuclides (Walker et al. [1989\)](#page-35-0). Tritium and Carbon-14 (along with a number of other radioactive nuclides) exist in the environment due to continuous production in the atmosphere by cosmic ray-induced reactions and as a consequence of thermonuclear explosions, operations of nuclear plants and other industrial outputs.

2.2.1 Tritium

The radioactive isotope of hydrogen $(3H)$ or T) is produced by a nuclear reaction between atmospheric nitrogen and thermal neutrons in the upper atmosphere (Libby [1946](#page-34-1)):

$$
^{14}\text{N} + \text{n} \rightarrow ^{12}\text{C} + ^3\text{H}
$$

The ${}^{3}H$ thus formed enters the hydrologic cycle after oxidation to ${}^{1}H^{3}HO$. It finally decays according to

$$
{}^{3}H \rightarrow {}^{3}He + \beta
$$

with $E\beta$ max = 18 keV and a half-life of 12.43 years (Unterweger et al. [1978](#page-34-2)).

Owing to the low probability of the nuclear reaction and short residence time (Rozanski et al. 1991) of ${}^{3}H$ in the atmosphere, the natural ${}^{3}H$ concentration in the air is very low. Low-level tritium concentrations are expressed in tritium unit (TU). One TU or TR (tritium ratio) corresponds to one tritium atom per 10^{18} atoms of hydrogen $(^{3}H/^{1}H = 10^{-18})$. A concentration of 1 TU is equivalent to a specific activity of 0.118 Bq/L of water.

Carbon-14

The natural occurrence of the radioactive carbon isotope, ^{14}C or radiocarbon, was first recognized by Libby [\(1946](#page-34-1)). It is naturally formed in the transitional region between the stratosphere and troposphere about 12 km above the Earth's surface through the nuclear reaction:

$$
^{14} N + n \rightarrow ^{14} C + p
$$

The thermal neutrons required are produced by reactions between very high-energy primary cosmic ray protons. 14C decays according to

$$
^{14}C \rightarrow ^{14}N + \beta ^{-}
$$

with a maximum β ⁻ energy of 156 keV and a half-life of 5730 ± 40 years (Godwin [1962\)](#page-33-2). Molecules of the atmospheric 14C thus formed very soon oxidize to 14CO and ultimately to $^{14}CO_2$, which mixes with the inactive atmospheric CO₂. $^{14}CO_2$ molecules enter the oceans and living marine organisms. Some are also assimilated by land plants, so that all living organisms, vegetable as well as animal, contain ^{14}C in concentrations about equal to that of atmospheric $CO₂$. The production and distribution of 14C in nature occur through series of chemical and biological processes, which has become stationary throughout much of geologic time. As a consequence, the concentration of 14C in the atmosphere, oceans and biosphere reached a steadystate value, which has been almost constant during a geologic period, which is long compared to the life span of a ¹⁴C nucleus. This natural concentration, ¹⁴C/¹²C, is of the order of 10−12, which is equivalent to a specific activity of about 0.226 Bq/gC (13.56 disintegrations per minute per gramme of carbon).

It is extremely difficult to make an absolute measurement of a ^{14}C activity. Therefore, the sample activities are compared with the activity of a standard under equal conditions. This results in a ^{14}C activity ratio or ^{14}C concentration ratio:

$$
^{14}a = \frac{^{14}A_{\text{sample}}}{^{14}A_{\text{reference}}} = \frac{^{14}A}{^{14}A_{\text{R}}} = \frac{^{14}C_{\text{decay rate in the sample}}}{^{14}C_{\text{decay rate in the reference}}} = \frac{^{14}C_{\text{concentration in the sample}}}{^{14}C_{\text{concentration in the reference}}}
$$

The symbol 14A may be used for the 14C content (radioactivity or concentration) of a sample, whether the analytical technique applied is radiometric or mass spectrometric (AMS). Under natural circumstances, the values of 14A are between 0 and 1. In order to avoid the use of decimals, it is a general practice to report these values in %, which is equivalent to the factor 10−² . Thus, 14C activity can be calculated in percent modern carbon (pMC), whereas 100 pMC = 13.56 dpm/g of carbon. Knowing the rate of radioactive decay (λ or $T_{1/2}$), the age (T = time elapsed since death) of a carbonaceous sample, organic or inorganic, can be calculated from the measured activity, ¹⁴A, if the ¹⁴C activity at the time of death, ¹⁴A_{initial}, is known using the following equation:

$$
t = (t_{1/2} / \ln 2) \times ({}^{14} A_{\text{initial}} / {}^{14} A)
$$

3 Environmental Isotopes in Hydrological Cycle

The global hydrologic cycle is the vastly, complex dynamic process which transfers all phases of water molecules (gas, liquid and solid) through the atmosphere, land and oceans. Tracers provide a convenient way of obtaining space-time integrals of motion of water molecules over both large and small ranges of space and time. It is now well recognized that several stable $(^{2}H, ^{3}He, ^{11}B, ^{13}C, ^{15}N, ^{18}O, ^{34}S, ^{37}Cl, ^{87}Sr,$ etc.) as well as naturally produced radioactive isotopes $(^{3}H, {}^{14}C, {}^{36}Cl, {}^{39}Ar, {}^{85}Kr$ and U-disequilibria which includes the large progeny of decay schemes for the parents 238 U, 235 U and 232 Th) can be used to study the hydrological cycle. Stable isotopes $(^{2}H, ^{13}C, ^{18}O)$ and radioactive isotopes ³H and ¹⁴C are routinely applied to investigate or identify groundwater or surface water-related problem. Sometimes other isotopes mentioned above are also employed for a specific hydrological solution which cannot be solved by routinely used isotopes.

3.1 Stable Isotopes of Oxygen and Hydrogen

Both hydrogen and oxygen consist of a number of isotopes, whose variations in natural water are the basis for applying the isotope methodology in hydrology. Water is evaporating from the sea. The marine vapour for a large part precipitates over the oceans, as it is transported to higher latitudes and altitudes, where the

vapour cools down and condenses. Part of the vapour is brought to the continents where it precipitates and forms different modes of surface water and groundwater. The 'last' marine vapour is precipitated as ice over the Arctic and the Antarctic. Compared to the waters of the ocean, the meteoric waters (i.e. the atmospheric moisture, the precipitation and groundwater and surface water derived from them) are mostly depleted in the heavy isotopic species: ^{18}O , ^{17}O and ^{2}H . The main reason for depleted values of meteoric water is the Rayleigh rainout effect, operating on a limited water (vapour) reservoir in the atmosphere. The average ocean composition is accepted as the reference standard for these isotopes so that $\delta S MOW = 0\%$ by definition (Craig [1961b\)](#page-33-3). The δ values of the meteoric waters are thus negative numbers.

Global distribution of isotopes was established by the IAEA in co-operation with WMO in 1961. In this programme, monthly pooled samples of precipitation were collected worldwide and then analysed for their ${}^{18}O$, ${}^{2}H$ and ${}^{3}H$ content. The degree of depletion is related phenomenologically to geographic parameters such as latitude, altitude and distance from the coast and to the fraction precipitated from a vapour mass content. From $\delta^{18}O$ and δ^2H values in meteoric waters derived from the data of GNIP (the Global Network of Isotopes in Precipitation), the following observation have been made:

- (a) A gradual decrease of the heavy isotopic concentration when going from lower to higher latitude (latitude effect).
- (b) A decrease in $\delta^{18}O$ and δ^2H when going from coast to a continent land (continental effect).
- (c) A decrease in $\delta^{18}O$ and δ^2H content with increasing altitude (altitude effect).
- (d) Seasonal variation of $\delta^{18}O$ and δ^2H is related to seasonal variation in temperature (seasonal effect).

3.1.1 δ18O and δ² H Correlation

The changes of ¹⁸O and ²H concentrations in meteoric waters were shown to be fairly well correlated (Friedman [1953;](#page-33-4) Craig [1961a](#page-33-5); Dansgaard [1964;](#page-33-6) Yurtsever [1975\)](#page-35-1) so that in the (δ^2 H, δ^{18} O) graph, the isotopic compositions of precipitation are aligned along what is referred to as a meteoric water line (MWL) for which a global average is $\delta^2 H = 8 \delta^{18}O + 10\%$ (then called the GMWL). The variations in $\delta^{18}O$ and δ2 H can be better understood by considering the two main processes in the global water cycle: (i) evaporation of surface ocean water and (ii) the progressive raining out of the vapour masses as they move towards regions with lower temperatures, i.e. higher latitudes and altitudes.

3.1.2 18O and 2 H in Groundwater

Meteoric ¹⁸O and ²H signal is transferred to groundwater during recharge. For many groundwaters, their isotopic composition will equal the mean weighted annual composition of precipitation. For others important deviation from precipitation is found. It also sheds light on the mechanism of recharge. Unlike temperate regions, the isotopic composition of groundwater in arid regions can be considerably modified from that of local precipitation. The cause is the strong isotopic enrichment in water during evaporation. However, characteristic trends imparted by evaporation can be useful in understanding the mechanism of recharge, as well as determining recharge rates. Initial stable isotope composition can also be modified by exchange with oxygen-bearing and possibly hydrogen-bearing mineral. This exchange is of importance in geothermal environments. Another process, which may modify the initial stable isotope content of groundwater, is the isotopic exchange with a gas phase, which is not initially in equilibrium with the environmental water. The distinctive and characteristic stable isotopic composition of waters from different geographic origin or of different hydrological nature on one hand and their conservative property on the other hand form the basis for their application in hydrological studies.

3.2 Stable Isotope of Carbon (13C)

The chemical element carbon has two stable isotopes, ¹²C and ¹³C. Their abundance is about 98.9% and 1.1%, so that the ¹³C/¹²C ratio is about 0.011 (Nier [1950](#page-34-4)). As a result of several fractionation processes, kinetic as well as equilibrium, the isotope ratio shows a natural variation of almost 100‰. The least depleted atmospheric $CO₂$ had originally δ^{13} C values near -7% . Since the nineteenth century, this value has undergone relatively large changes. In general, high values are observed in oceanic air far removed from continental influences and occur in combination with minimal $CO₂$ concentrations. More negative δ^{13} C values are found in continental air and are due to an admixture of CO₂ of biospheric and anthropogenic origin ($\delta^{13}C \approx -25\%$), in part from the decay of plant material and in part from the combustion of fossil fuels (Keeling [1958](#page-34-5); Mook [1983\)](#page-34-6). Plant carbon has lower ¹³C content than the atmospheric $CO₂$ from which it was formed. The fractionation, which occurs during $CO₂$ uptake and photosynthesis, depends on the type of plant and the climatic and ecological conditions. As complicated biogeochemical processes are involved in the degradation of terrestrial and marine plant material ultimately into coal, oil and natural gas, the range of $\delta^{13}C$ values of these fossil fuels is larger, extending to more negative values, especially of biogenic methane.

3.2.1 13C Variations in Groundwater

Soil CO2 is important in establishing the dissolved inorganic carbon content of groundwater. After dissolution of this CO2, the infiltrating rainwater is able to dissolve the soil limestone:

$$
CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-
$$

Because limestone generally is of marine origin ($\delta^{13}C \approx +1\%$), this process results in δ**13C** of the dissolved bicarbonate of about −11 to −12‰ (in temperate climates). In the soil the HCO3− first formed exchanges with the often present excess of gaseous CO₂, ultimately resulting in $\delta^{13}C = -16\%$. In surface waters such as lakes, 13C enrichment of dissolved inorganic carbon can be caused by isotope exchange with atmospheric CO₂ ($\delta^{13}C \approx -7.5\%$) ultimately resulting in values of $\delta^{13}C = +1.5\%$, identical to oceanic values. Consequently, freshwater carbonate minerals may have 'marine' $\delta^{13}C$ values. In these cases the marine character of the carbonate is to be determined by $\delta^{18}O$. In addition to HCO3⁻, natural waters contain variable concentrations of CO_2 which leads to lowering in $\delta^{13}C$ value of DIC than that of the bicarbonate fraction alone. Hence, $\delta^{13}C(DIC)$ in groundwater (Vogel and Ehhalt [1963](#page-35-2)) and in stream and river waters derived from groundwater are generally in the range of -12 to -15% .

3.3 Radioisotope of Hydrogen (3 H)

The natural production by cosmic rays results in a steady-state inventory on the Earth's surface of about 3.5–4.5 kg of tritium (Lal and Peters [1967](#page-34-7); O'Brien et al. [1992\)](#page-34-8) most of which is present as part of water molecule $(H₂O)$. As part of water molecules, tritium follows the pathway through the hydrologic cycle almost exactly, with only small perturbation due to fractionation effects during phase changes (Bigeleisen [1962](#page-33-7)). These fractionations are very small and can be ignored relative to measurement uncertainties and larger change resulting from radioactive decay.

Pre-bomb tritium concentrations are not well known, though some estimates available suggest they were of the order of 2–8 tritium units across US continent (Thatcher [1962](#page-34-9)). Tritium concentrations in precipitation rose rapidly following the atmospheric bomb test and were found to have a strong dependence on location and season. Tritium concentration in precipitation peaked in the northern hemisphere during 1963 (Fig. [1](#page-9-0)), rising to a few thousand units in most mid-continental location (IAEA [1981,](#page-33-8) [1992\)](#page-34-10), whereas ³H levels in atmospheric waters in the southern hemi-sphere (Fig. [2](#page-9-1)) were lower than at comparable north latitude stations. This is a reflection of the predominant northern location of weapon testing sites and the slow inter-hemispheric transport of tracers.

Fig. 1 Smoothed curve representing the average ³H content of precipitation over the continental surface of the northern hemisphere

Fig. 2 Latitudinal distribution of tritium content in monthly precipitation for oceanic (inland and coastal) stations of the IAEA/WMO global network

3.3.1 Tritium in the Groundwater

The most important use of tritium as a hydrologic tool is in the study of residence times of surface water and groundwater. Groundwaters and surface expressions of groundwaters such as small springs and seeps have the widest range of tritium concentration of any type of water.

They are also the systems to which tritium has been applied most extensively. At the simplest level, the presence of tritium in groundwater implies that at least a fraction of water in the aquifer has been recharged since the beginning of the bomb era. Approximate age ranges can be given for groundwater samples if one assumes that the highest concentrations represent the tritium peak (Fontes et al. [1980](#page-33-9)). During recent years, the atmospheric reservoir has been practically exhausted of the ³H introduced by the nuclear tests so that the atmospheric 3 H levels have almost returned to the pre-1952 levels, except for some local anthropogenic releases of ³H from the nuclear industry and other uses of tritiated materials. To obtain more information from the tritium data, it is desirable to have a time series of tritium data over decadal time scales. Over the years a series of model and approaches have been developed to work with these sets of data.

3.4 Radioisotope of Carbon (14C)

The production of 14 C obeys the same laws as tritium as far as latitude is concerned, but because of its oxidation to gaseous form of $CO₂$ and long residence time in the troposphere, 14 C is much more efficiently mixed in the troposphere. 14 CO₂ of the troposphere dissolves in the ocean or is consumed by vegetation during photosynthesis. Decay of vegetation and root respiration return much of the 14C to the atmosphere. The largest storehouse of 14C is by far oceans, in the form of HCO3− (Berner and Lasaga [1989](#page-33-10)). Accumulation in the troposphere and the hydrosphere/biosphere is balanced by radioactive decay and burial. This balance or secular equilibrium is relatively robust over the short periods (decades to 100s years) and amounts to an atmospheric concentration of ¹⁴CO₂ on the order of 10^{-2} of the total concentration of CO2. This 14C activity is defined as modern 14C and is the basis of the radiocarbon standard. This secular equilibrium can be altered by natural processes and manmade activities.

While the industrial age has been pumping dead carbon into the atmosphere and diluting atmospheric 14C, the nuclear age has been creating it. Since the 1950s, atmospheric weapon testing and nuclear power plants have been realizing additional radiocarbon to the atmosphere and biosphere. The strong increase in the atmospheric 14C level due to the nuclear test explosions is of more relevance to the hydrologist. During the bomb explosions, ^{14}C (and ^{3}H) is being produced by the same nuclear reactions that are responsible for the natural production. In the northern hemisphere, the peak concentration occurred during the spring of 1963, when it

Fig. 3 Curve representing the natural ¹⁴C content of atmospheric CO2 during test explosions of nuclear weapons

was about double the natural concentration (Fig. [3](#page-11-0)). In the southern hemisphere, a more gradual increase has taken place.

3.4.1 14C in Groundwater

From the atmospheric reservoir, neglecting the direct dissolution of CO2 in rainwater, which will not lead to more than a few ppm of total dissolved carbon, CO2 enters into the water cycle by two main processes:

1. Chemical process: It is the process of dissolution buffered by solid carbonate saturation. The following chain of reactions takes place in free waters:

$$
CO2(gas) \Leftrightarrow CO2(aqueous)\nCO2(aqueous) \Leftrightarrow H2CO3\nH2CO3 \Leftrightarrow HCO3- + H+\nHCO3- \Leftrightarrow CO232- + H+\nCO3- + Me2+ \Leftrightarrow MeCO3
$$

where Me²⁺ is generally Ca²⁺ but can include Mg²⁺, Fe²⁺ and sometimes $2Na^{+}$ in highly saline continental brine.

2. Biochemical production: The assimilation of atmospheric $CO₂$ by plants through photosynthesis is accompanied by the release of $CO₂$ in the soil zone. This occurs by fermentation and decay of organic matter (fulvic, flavic, and humic acids) but mainly by respiration in soil root zone. It is the soil zone that gives the recharging groundwater its radiocarbon signal. Commonly the $CO₂$ partial pressure in soil

exceeds a value of 10^{-2} atm. This biogenic CO_2 then gives total dissolved inorganic carbon according to several processes depending upon local geological conditions.All of these processes which produce large amount of HCO3− or CO32− can be divided into:

- 1. Those in which all dissolved carbon is of inorganic origin.
- 2. Those in which the dissolved carbon comes from both biogenic $CO₂$ and solid carbonate. For the former, the 14C activity of TDIC will exclusively reflect that of $CO₂$ source; for the latter the ¹⁴C activity of biogenic $CO₂$ will be diluted by the carbon coming from the leaching of solid carbonate since it is generally very old and thus inactive. The chemical dilution of ${}^{14}C$ in the TDIC may be observed even in non-carbonate situations (Fritz et al. [1978](#page-33-11)). The consequence is that age estimation of TDIC cannot simply be done using the modern activity (100 pMC).

4 Case Studies

4.1 Application of Environmental Isotopes to Identify Landfill Leachate Contamination: Gazipur Landfill, New Delhi, India

4.1.1 Introduction

The world urban population was about 1.52 billion in 1975, increased to 2.84 billion in 2000, and is projected to 4.91 billion by 2030 (United Nation [2006\)](#page-34-11). In the past, municipal garbage dumps (sanitary landfills are only a recent technology) were unlined and sited with little regard to local hydrogeology. Groundwater contamination is one of the major problems associated with improper waste disposal. Leaching of hazardous elements in the groundwater in surrounding areas of landfill sites is reported from different sanitary landfill sites all over the world (Harris and Parry [1982;](#page-33-12) Harris and Lowe [1984](#page-33-13)). One of the most significant impacts of a landfill has been consistently identified as arising from leachate (Farquhar [1989](#page-33-14); CAE [1992;](#page-33-15) Mulvey [1997](#page-34-12)). Environmental isotopes are being extensively used for investigating landfill sites and tracing pollution plumes. Leachate with high dissolved organic carbon (DOC) will generate large quantities of these gases. The isotopic fractionations associated with these bacterially mediated reactions are huge. Values of $\delta^{13}C$ and δ^2 H in the reaction products fall outside of the range associated with natural water. Most landfills where strong methane production occurs have co-existing $CO₂$ or dissolved inorganic carbon (DIC) that is enriched in 13C (Lansdown et al. [1992\)](#page-34-13). Hackley et al. ([1996\)](#page-33-16) provided evidence that methanogenesis occurring in the landfills leads to unique ^{13}C isotopic signature identifiable in leachate samples. Tritium activity present in landfill leachate provides useful tracer in the study of landfill site. Luminescent paint that contains tritiated hydrocarbons is considered as the most probable source of tritium in landfill leachates.

Fig. 4 Map of India showing Delhi and landfill sites in the National Capital Territory of Delhi

4.1.2 Gazipur Sanitary Landfill (SLF) Site, New Delhi

The quantity of municipal solid wastes generated in Delhi has been consistently rising over the years. This can be attributed to the rapid population growth, mass migration of population from rural to urban areas, increase in economic activities in general in the city and the change in lifestyle of the people. The continuous generation of solid waste has developed several landfill areas (Fig. [4\)](#page-13-0), and the land is retrieved for various purposes. There are two major categories of landfills in Delhi:

- 1. Landfills completed and retrieved land is used for various purposes.
- 2. Active landfills where present filling is taking place.

Gazipur is an active landfill site and the total area of the site is 70 acres. Filling in this landfill site commenced in 1993, and the service zones for this landfill site are East Delhi, New Delhi and Central Delhi. This site was selected for the present study and environmental stable isotopes ${}^{18}O$, ${}^{2}H$ and ${}^{13}C$, and radioactive isotope ${}^{3}H$ has been used to find out the contamination of groundwater by landfill leachate and direction of the flow of the leachate as well as extent to which the leachate has moved.

Leachate sample from Gazipur landfill site was collected for isotopic ($\delta^{18}O$, δD , δ13C and 3 H) and chemical analysis in the post-monsoon (November 2003) period. Groundwater samples in the vicinity of landfill site were collected for environmental isotopes as well as chemical analysis during post-monsoon (November 2003) and pre-monsoon (June 2004) period. Sampling points have been represented as circle in the site plan map (Fig. [5](#page-14-0)).

Fig. 5 Site plan map of Gazipur landfill site showing locations of sampling points

The landfill site is situated 8 km east of river Yamuna and about 0.5 km north of Hindon canal. About 10 m thick landfill materials had been dumped in this site till study period. The area is underlain by quaternary alluvium of about 134 m thick below which weathered and fractured quartzite is present. The area is underlain by fine to medium sand mixed with coarse hard kankar up to a depth of 50 m. Thus, on macro-level it can be inferred as a single aquifer system of depth 50 m only. Lenses of minor clayey silt horizons are also present within this sand horizon at a few places. Sediments below this depth are predominantly clayey in nature.

4.1.3 Results and Discussion

Electrical conductivity of almost all the samples is less than 2000 μS/cm that is below the permissible level (Bureau of Indian Standards) except GZ-7, GZ-3 and GZ-1. Since GZ-1 is situated opposite to the direction of the flow from landfill site, quality of groundwater at this location may be in situ groundwater quality at 30 m depth. High concentration of iron has been found in GZ-3, GZ-10 and GZ-11 samples. High concentration of Fe in GZ-3, GZ-10 and generally low nitrate concentrations in all groundwater near landfill site could be due to percolation of landfill leachate. Usually leachate generation is favoured by reducing condition. Therefore,

Fig. 6 δ^{18} O vs. δ^2 H plot of post-monsoon samples

leachate contaminating groundwater may show low nitrate content as it may undergo anaerobic reduction at various redox zones. Heavy metals Cr, Ni, Zn and Cd concentrations in the leachate are relatively low as compared to the amount of refuse. It could due to natural attenuation of heavy metals in landfill leachate. Negligible concentrations of heavy metals in groundwater in the vicinity of landfill do not give any indication of leachate contribution to the groundwater.

The leachate sample GZ-6 is highly enriched in ^{18}O and ^{2}H isotopes compared to nearby groundwater samples (Figs. [6](#page-15-0) and [7\)](#page-16-0). Fritz et al. [\(1991](#page-33-17)) have shown similar results in their study. Most of the groundwater samples fall along the meteoric water line. GZ-7, GZ-8, GZ-9 and GZ-10 samples located at the southeast side of the landfill are slightly enriched in stable isotope ¹⁸O and ²H than other groundwater samples. It could be due to movement of pollution plume from landfill leachate towards southeast of landfill site. In general post-monsoon samples are slightly depleted than pre-monsoon samples. It could be due to high rainfall during monsoon period in Gazipur area.

The tritium content of rainwater of Delhi during monsoon period of the study was found to be about 8 TU. High tritium content of about 102 TU has been found in Gazipur landfill leachate sample. Liu et al. ([1992\)](#page-34-14) have also found the unique tritium relative to the surrounding groundwater in their study. Plots of $\delta^{18}O$ vs. tritium (Figs. 8 and 9) show that GZ-2, GZ-3, GZ-4, GZ-7 and GZ-11 are above 10 TU in post-monsoon samples indicating contribution from leachate in all these samples. GZ-1 showing less than 2 TU seems to be unaffected from landfill leachate contamination. GZ-3, GZ-4 and GZ-7, which are close to landfill site, show significantly

Fig. 7 δ^{18} O vs. δ^2 of H plot of pre-monsoon sample

Fig. 8 δ^{18} O vs. ³H plot of post-monsoon sample

Fig. 9 δ18 O vs. 3 H plot of pre-monsoon sample

lower concentration of tritium in pre-monsoon period than post-monsoon period. It could be due to high rainfall during monsoon, which caused rapid leachate movement to these wells during and immediately after the monsoon season. Canal water collected in post-monsoon period showed 14 TU. The shallow wells GZ-15 (12 m deep) and GZ-13 (10 m deep) show tritium concentration of about 10 TU. High tritium content of GZ- 15 could be due to leachate contribution. GZ-13 located at northeast of landfill site may be getting high tritium concentration from drain water because stable isotope values do not support contamination from leachate. Similarly, high tritium content of GZ-11 may be due to adjacent drain in pre-monsoon time.

 δ^{13} C values of DIC of groundwater and leachate have been shown in Figs. [10](#page-18-0) and [11.](#page-18-1) 13C of leachate sample is highly enriched. Lansdown et al. [\(1992](#page-34-13)) and Hackley et al. [\(1996](#page-33-16)) have explained about enrichment in δ^{13} C of leachate. GZ-1 shows about −12‰ which could be the natural groundwater value unaffected by leachate. Thus, carbon-13 result further supports the tritium and stable isotope result. Enriched value of GZ-7 and GZ-15 indicates that these wells are being contaminated from landfill leachate. GZ-3 and GZ-4 samples are isotopically enriched in post-monsoon than pre-monsoon. It is once again an indication of rapid movement of leachate into GZ-3 and GZ-4 wells due to heavy rainfall during monsoon period. Enriched value of GZ-15 indicates that leachate has contributed to this well too. Depleted value of $\delta^{13}C$ of GZ-13 tells about the absence of leachate contribution towards the east side of the drain.

Fig. 10 δ^{18} O vs. δ^{13} C plot of post-monsoon sample

Fig. 11 δ^{18} O vs. δ^{13} C plot of pre-monsoon sample

4.1.4 Conclusion

Thus, on the basis of tritium, stable isotopes ^{18}O , ^{2}H and carbon-13 data supported by chemical and hydrological data, it can be concluded that leachate plume is moving in southeast direction as well as in south direction from landfill site. The pollution plume is moving beneath and across the canal, but it has not reached to Kondli village (GZ-16).

4.2 Investigation of Recharge Areas to the Springs Using Isotope Techniques as Well as Hydrogeology and Geomorphology in the Mountainous Region of Himalaya, Uttarakhand

4.2.1 Introduction

A spring is the result of an aquifer being filled to the point that the water overflows onto the land surface. They range in size from intermittent seeps, which flow only after much rain, to huge pools flowing hundreds of millions of gallons daily. The amount of water that flows from springs depends on many factors, including the size of the caverns within the rocks, the water pressure in the aquifer, the size of the catchment, and the amount of rainfall. Human activities also can influence the volume of water that discharges from a spring. Many of the current classification systems borrow heavily from the works of Bryan [\(1919](#page-33-18)) and Meinzer ([1923\)](#page-34-15) and incorporate parts of these systems and refine or expand portions based on modern quantification and knowledge of springs. Meinzer, in 1923, proposed a classification of springs based on the discharge of the spring. Mountainous region of Uttarakhand (Fig. [12\)](#page-20-0) has a large number of perennial as well as ephemeral springs. These springs are mainly non-artesian springs. Majority of them are sixth and seventh magnitude springs and have seepage type outlet. Owing to anthropogenic activities, most of the springs in the mountainous region of Uttarakhand show reduced or negligible discharge during summer season. The present study aims to identify the recharge zones for the springs, to study various hydrological processes in this region and to evaluate the feasibility of artificial recharge to increase discharges of springs in dry period.

4.2.2 Study Areas

Four sites, one each from Dehradun (Pipaya) and Uttarkashi (Brahmkhal) and two in Rudraprayag (Isala and Kakodakhal) districts of Uttarakhand (Fig. [12](#page-20-0)), were selected for the investigation. Pipaya site is located about 80 km away from Dehradun towards north direction. There are 11 springs in this site located in 2 main valleys and 1 spring in each of 3 sub-valleys with elevations ranging from 1350 to

Fig. 12 Districts map of Uttarakhand and location of the selected sites

1650 m above mean sea level (amsl), and discharges of these springs vary from 0.1 to 22 l/min. Brahmkhal area belongs to Uttar Kashi district located about 40 Km southwest of Uttar Kashi city. There are eight springs present in two valleys, and the elevation of these springs ranges from 1200 to 1760 m amsl. The minimum and maximum discharges of the springs are 0.5 and 30 l/min. Isala area is located in Rudraprayag district of Uttarakhand state, and there are four springs situated in one valley between elevation 1250 and 1450 m amsl. Kakodakhal site is also located in Rudraprayag district of Uttarakhand state and falls north of river Alaknanda. There are five springs located in one valley, and the elevation of these springs ranges from 720 to 920 m amsl.

Geology of Pipaya project site is characterized by mostly slates interbedded with siltstones and phyllites with minor quartz, and this area has an average rainfall of 2100 mm per year from 2004 to 2009. In Brahmkhal, the entire area is covered by hard rock, and the main rock types are quartzites, phyllites, slates, and gneisses of varying degrees of metamorphism along with granite intrusive and metabasics. The

rocks have undergone intensive metamorphism and recrystallization. This area has an average rainfall of 1690 mm per year from 2004 to 2009. In the case of Isala and Kakodakhal, the lithological sequence belongs to Rudraprayag Formation of Garhwal Group (late Precambrian to Cambrian age) and is characterized by argilloarenaceous facies. The average rainfall is found to be 930 mm per year from 2004 to 2009. However, all the project sites have received very high rainfall during 2010, and the increase in rainfall varies from 50% to more than 200%.

4.2.3 Results and Discussion

Four sets of spring water samples were collected from the above-mentioned sites during February, June, September and November of the year 2009 for physicochemical, chemical and isotope measurements. In addition to spring water, rainwater samples were also collected during 2009 and 2010 at each site from different altitudes.

Spring water quality was found to be fresh with electrical conductivity less than 350 μS/cm and neutral to slightly alkaline at all the project sites. Based on Piper's classification, the spring waters are of Ca-Na-HCO3 and Ca-Mg-HCO3 types, and there is a change in water types in different seasons. The change was most significant in the case of Isala and Kakodakhal sites. The variation in chemical type can be attributed to the diverse lithology of the formation as well as increased leaching of the minerals due to relatively long residence times of the spring waters.

 δ^2 H versus δ^{18} O was plotted for rainwater samples from all the four project sites, and local meteoric water lines (LMWLs) were drawn for all the four sites. Most of the spring water samples fall slightly below the local meteoric water line in the case of δ^2 H versus δ^{18} O plots, indicating that major component of spring water is local precipitation. It is observed that $\delta^{18}O$ stable isotope composition of spring waters collected during February 2009 is most depleted among the four sets, suggesting the contribution of winter precipitation. However, all the samples collected during February 2009 from all the four sites fall above the LMWL due to enriched values of δ^2 H. It seems there may be measurement error of δ^2 H values for February 2009 samples.

The variation of rainwater isotopic composition of Pipaya samples with respect to altitude is shown in Fig. [13](#page-22-0). An altitude effect is found, and it is estimated to be 0.37‰ δ¹⁸O per 100 m elevation. In the plot altitude versus $\delta^{18}O$ (Fig. [14a](#page-23-0)), there is no correlation found in springs waters of valley 1. Most of these springs fall within a narrow altitude range of \sim 100 m (i.e. from 1350 to 1460 m amsl); therefore, altitude effect in isotope composition has not been observed. In valley 2 of this site, there is no correlation found between altitude and δ^{18} O as shown in Fig. [14b](#page-23-0) except the depleted values of February 2009 which show altitude effect.

From the δ^{18} O variation of rainwater of Brahmkhal with respect to altitude, it has been found that δ^{18} O are more and more depleted with increase in altitude, and from the slope of the best fit line, altitude effect is calculated to be 0.4% δ^{18} O per 100 m elevation (Fig. [15\)](#page-24-0).The spring water samples of valley 1 collected during February

and June 2009 show altitude effect of -0.2% δ^{18} O per 100 m which is within the values reported in the literature (Zuppi et al. [1974](#page-35-3); Shivanna et al. [2008](#page-34-16); Navada [1988\)](#page-34-17). The altitude effect is not seen in the case of September and November 2009 samples (Fig. [16a\)](#page-25-0) which could be due to the contribution of rainwater from different altitudes. In valley 2, altitude effect is seen in all sets of samples shown in Fig. [16b](#page-25-0). In this case, the altitude effect is different for different months, and it is found to vary from −0.15‰ to −0.28‰ per 100 m elevation.

Variation of $\delta^{18}O$ values of rainwater of Isala collected during 2010 with altitude shows no correlation, as shown in Fig. [17](#page-26-0). In fact the highest and lowest altitude rainwater samples show similar isotopic values. A similar trend has been found in spring water of all seasons of 2009 (Fig. [18](#page-26-1)).

The variation of δ^{18} O of Kakodakhal rainwater sample collected in 2010 with altitude shows depletion in $\delta^{18}O$ value with increase in altitude (Fig. [19](#page-27-0)). The altitude effect is calculated to be −0.54‰ per 100 m elevation. In the case of spring waters collected during February and November 2009, there is no correlation between altitude and $\delta^{18}O$, whereas June and September spring water samples show altitude effect with different slopes of -0.2% and -0.5% , respectively, shown in Fig. [20](#page-27-1). High rainfall in the month of August/September causes high spring discharges without undergoing appreciable evaporation, whereas evaporation effect causes low altitude effect in the month of June.

Environmental tritium content of the rain water samples show about 8 TU. In general the spring samples of four sites have tritium in the range of 6.5–8.5 TU. It clearly indicates that all the spring waters are freshly recharged precipitation water.

Fig. 14 (**a**, **b**) Altitude versus δ18O composition of spring water samples collected in different valleys; (**a**) valley 1 and (**b**) valley 2

Fig. 15 Altitude versus δ^{18} O composition of rain water samples collected during 2010

4.2.4 Conclusion

Based on the isotope hydrogeochemical investigations, the following conclusions can be drawn:

- All the spring waters are freshly recharged precipitation water.
- Contribution of winter monsoon is observed in February spring discharges at all sites.
- During the peak monsoon periods (August/September), various subsurface channels contribute to the spring discharges leading to high discharges and wide variation in isotopic content.
- In Pipaya, no altitude effect in isotope content of spring waters is observed, so exact altitude of recharge zones of the springs could not be established using environmental isotopes; however, using local geology and geomorphology, it can be inferred that the recharge altitude is about 1700 m amsl for V3S1 and V4S1, whereas for the rest of the springs, it may vary from 1400 to 1600 m amsl.
- In Brahmkhal, altitude effect was found. Based on altitude effect and geomorphology, it can be inferred that the recharge zone for high altitude springs of both valleys is 1900 m amsl and for low altitude springs, it is 1500 m amsl.
- In Isala, the variation of spring altitudes is about 200 m so no altitude effect was observed. It can be inferred from isotope and hydrochemistry that the springs are recharged by local precipitation and based on geomorphology, recharge altitude was found to be 1600 m amsl.
- In Kakodakhal, based on altitude effect and geomorphology, the recharge area was found to be 1100 m amsl for the springs except one whose recharge areas were found to be 800 m amsl.

Fig. 16 Altitude versus δ18O composition of spring water samples collected in different months; (**a**) valley 1 and (**b**) valley 2

Fig. 18 Altitude versus δ18O composition of spring water samples collected in different valleys

Fig. 19 Altitude versus δ¹⁸O composition of rain water samples collected from Kakodakhal site during September 2010 monsoon

Fig. 20 Altitude versus δ18O composition of spring water samples collected in different months from Kakodakhal site

4.3 Application of Environmental Isotopes in Identifying Source of Seepage Water in the Basement in Some Parts of Jodhpur City, India

4.3.1 Introduction

Seepage water accumulation in the basement of a number of buildings and rise in the static water level (SWL) has been reported in March 1998 in some parts of Jodhpur city. With the availability of water from Rajiv Gandhi Lift Canal located about 209 km from the city, feeding of Kaylana Lake by canal water started in 1998. Jodhpur gets a water supply of about 200 million litres daily. The main source of water supply to the city is from Rajiv Gandhi Lift Canal. Hence, the use of water impounding structures and groundwater has been reduced significantly. Bacteriological analysis has revealed the presence of coliform above permissible limit in all the water samples irrespective of seepage water and groundwater. However, faecal coliform (*E. coli*) is absent in all the samples including basement samples. An isotopic study was carried out to find out the source of seepage in March 2000. Difference in isotopic characteristics of water from different sources helped to understand the source of seepage.

4.3.2 Study Area

Jodhpur is an important city located in the state of Rajasthan of India. It is located at the edge of the Thar Desert and situated at 26°17′N latitude and 73°02′E longitude. It has an average elevation of 232 m. The climate of Jodhpur is generally hot and arid. The amount of rainfall increased tremendously in Jodhpur city and was primarily designed to arrest rainwater in impounding structures to provide sustained water supply to the populace. The city consists of a number of water impounding structures called baories. Seepage from these structures was exploited through a number of wells and step wells. Before 1998 groundwater was the main source of water supply through impounding structures or bore wells. Kaylana Lake in the Jodhpur city was also used for drinking water supply. A rise in the static water level (SWL) ranging from 0.01 to 3 m was noticed in different parts of the Jodhpur city mainly in the old city area. Rise in SWL caused seepage of water in the basement of a number of buildings in some parts of Jodhpur city (Kunj Bihari Ka Mandir and Sojati Gate areas). Kaylana Lake is situated at the higher elevation than the seepage area. Hence, it is believed that there may be direct hydraulic continuity of Kaylana Lake with the seepage area. Increase in the level of Kaylana Lake, due to feeding from the lift canal to meet the demand of the rising urban population, may be responsible for increase in SWL and hence seepage in the basement.

Jodhpur city area that includes areas affected by seepage consists of mainly alluvium and rhyolite, whereas Kaylana Lake area, situated about 10 km on the western side of the city (Fig. [21](#page-29-0)), consists of fractured rhyolite. A massive rhyolite ridge is

Fig. 21 Location and geological map of Jodhpur city and surrounding areas

running from northeast to southwest between Kaylana Lake and city area. Northern and eastern peripheries of the Jodhpur city consist of alluvium and sandstone. Water samples from wells fitted with hand pumps, basement, lake, filter houses, baories and ponds were collected for environmental isotopes (oxygen-18, deuterium, tritium) as well as chemical analysis in March 2000.

Figure [22](#page-30-0) shows reduced levels of different parts of the city. Reduced level of Kaylana Lake is 280 m amsl, whereas reduced level of seepage locations is about 250 m amsl. The affected area is sloping from north to east and southeast. The hills on which the fort is located have higher elevation, and the relief is fairly steep. A number of surface water impounding structures were constructed in the immediate foothill zone and also at suitable location within the city to receive monsoon flows.

4.3.3 Results and Discussion

Chemical quality of water accumulated in the basement does not completely resemble that of the groundwater in wells in the immediate vicinity. EC of lake water from Kaylana Lake and filter houses is around 100 μS/cm since origin of this water is from lift canal. EC of the basement seepage water is less than the bore well and dug well water (groundwater) in the immediate vicinity. Similarly, EC of basement seepage water is less than the groundwater in the immediate vicinity. Therefore, it seems that the seepage water is a mixture of groundwater and lake water.

Fig. 22 Reduced level of seepage locations and Kaylana Lake, etc

Bore wells located at south of Kaylana Lake have lower EC than the groundwater near the seepage point. The same trend has been observed for major ion species. Bacteriological analysis (Report GWD [1998](#page-34-18)) has revealed the presence of coliform bacteria above permissible limit in all the water samples irrespective of seepage water and groundwater. However, faecal coliform (*E. coli*) is absent in all the samples including basement samples. Therefore, water from sewer line is not contributing to the seepage water. Thus, it is very difficult to infer the source of seepage water on the basis of chemical quality. Lake water is fed by the Rajiv Gandhi Lift Canal, and the source of canal water is a Himalayan river (River Satluj) originating from higher altitude and hence is highly depleted in $\delta^{18}O$ and $\delta^{2}H$ (Lambs [2000](#page-34-19); Singh and Quick [1993;](#page-34-20) Singh and Kumar [1996](#page-34-21); Singh et al. [1997\)](#page-34-22). Plot of $\delta^{18}O$ vs. δ^2H (Fig. [23\)](#page-31-0) shows that the water samples from lake and filter houses (which has been supplied by lake) are depleted in stable isotopes $\delta^{18}O$ and $\delta^{2}H$ compared to other surface water bodies like baori water and pond water due to Himalayan origin of the water feeding the lake. Pond water is highly enriched in stable isotopes $\delta^{18}O$ and δ2 H due to evaporation effect in desert conditions (Craig et al. [1956\)](#page-33-19). Baories are water impounding structure, which supplies water to nearby wells. Water from baories is slightly enriched than groundwater. $\delta^{18}O$ and δ^2H values of both baori water and groundwater fall near the global meteoric water line indicating that source of baori water and groundwater is recent precipitation. $\delta^{18}O$ and δ^2H value groundwater suggest that groundwater is recharged by modern precipitation without showing evaporation effect (Allison [1982](#page-33-20)) of desert condition. This can be due to the frac-

Fig. 23 Stable isotope composition of Jodhpur sample

tured rhyolite geological formation of the Jodhpur city area. Isotopic composition of basement samples fall between lake water and groundwater, which suggests that basement water is a mixture of lake water and groundwater. One spring sample (6) at Byas Park shows significantly depleted values of $\delta_{18}O$ and δ_2H indicating lake water as a major component of spring water, but its elevation (310 m) is greater than Kaylana lake which rules out the possibility of direct hydraulic continuity between lake and spring.

Tritium content of lake water and filter house water varies from 9 to 12 TU, whereas basement samples show tritium content of 6.5–10 TU (Fig. [24](#page-32-0)). Tritium content of bore well waters is in the range of 2.5–7 TU. Tritium values of groundwater suggest that groundwater contains major component of modern recharge. Groundwater sample, which is south of Kaylana Lake, shows tritium contents of 9.2 TU indicating that it may be getting some contribution from the lake. One groundwater sample from a hospital premise, which is far away from the old city (seepage location), shows very high value of about 15 TU. It seems that the tritium of groundwater is from hospital wastewater disposed off in open. Tritium concentration of spring water (-10 TU) at Byas Park suggests its similarity with lake water. Tritium content of basement samples (seepage water) varies from 7 to 9 TU. Tritium results also suggest that basement samples are mixture of lake water and groundwater. Tritium contents of baori water vary between 7 and 8 TU. Except two groundwater samples, all other groundwater, lake water baori water and spring water show tritium contents of more than 6 TU. Therefore, most of the water is recent water.

Fig. 24 Tritium contents of Jodhpur sample

4.3.4 Conclusion

On the basis of isotopic, chemical analysis and hydrogeological data, it can concluded that the lake water, which is supplied to the city, is contributing to the seepage water in the basement. The lake water contribution to the seepage could be either due to direct seepage from Kaylana Lake (due to the fractured nature of rhyolite) or seepage from pipelines (carrying lake water) and used water (waste water) percolating to the subsurface. Isotopic content of one spring sample is very close to lake water and the spring is situated at higher elevation than Kailana lake which is about 10 Km from the seepage locations and the spring. Therefore, direct hydraulic continuity of lake water to the seepage water is remote. The absence of *E. coli* in the entire basement samples rules out the possibility of seepage from sewer lines. Engineers from the drinking water supply department could not find any breakage in the water-carrying pipelines in Jodhpur city particularly in the seepage locations. Therefore, lake water contribution through this mechanism is also remote. Old Jodhpur city (seepage location) does not have very planned sewage system. Used water (waste water) supplied from Kaylana lake percolating to the subsurface seems to be the most probable mechanism of lake water contribution to the groundwater. Open dumping of wastewater and low permeability aquifer in the area particularly the old city area of Jodhpur caused the rise in the static water level (SWL) and hence seepage in the basement of building. After availability of water from the lift canal,

which is fed to Kaylana Lake, consumption of lake water increased, and groundwater consumption decreased. Therefore, increased consumption of lake water and discontinuation of groundwater withdrawal have further aggravated the seepage situation in the area.

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